Statistical Thermodynamics in Chemistry and Biology

14. Equilibria between liquids, solids, and gases

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Phase equilibria are described by the chemical potential

This chapter:

- ▶ A lattice model of pure solids and liquids is explored.
- ▶ Vapor pressures over liquids
- ▶ Processes of boiling and sublimation
- ▶ Surface tension from the equilibrium between bulk (interior) and the surface.
- ▶ Foundation for treating mixing and solvation (Chapters 15 and 16)

Why do liquids boil?

- ▶ Vapor is treated as an *ideal gas*.
- ▶ Balance between two *driving forces*.
  - ▶ Attractive *intermolecular interactions* hold the molecules together in the liquid phase.
  - ▶ The particles gain *translational entropy* when they escape to the vapor phase.
  - ▶ The free energy is minimized,

  $$\Delta G = \Delta H - T\Delta S \qquad \text{or} \qquad \Delta F = \Delta U - T\Delta S$$

  - ▶ The molecules prefer the liquid phase at low temperatures, and the vapor at high temperatures.

Why do liquids boil?
Part 2

- ▶ Exactly the same procedure as for chemical equilibria.
- ▶ N_c particles in the condensed phase, and N_v particles in the vapor phase.
- ▶ Regard p, T and N as constant,

$$dG = \mu_v dN_v + \mu_c dN_c \; ; \qquad dN_v + dN_c = dN = 0$$

- ▶ At equilibrium,

$$dG = (\mu_v - \mu_c) \, dN_v = 0 \qquad \Rightarrow \qquad \mu_v = \mu_c$$

- ▶ The vapor is regarded as an ideal gas, Eq. 11.50,

$$\mu_v = k_B T \ln \frac{p}{p_{\text{int}}^o}$$

Why do liquids boil?

Part 3: solids and liquids

▶ Regard a liquid or a solid as a lattice of *single-type* particles, see figure.

▶ Gases are around a factor 1000 less dense than a liquid; a liquid is around 10% less dense than a solid.

▶ Here we neglect the distinction between liquids and solids.

▶ Several approximations: liquids do not have long-range order (periodicity), the number of nearest neighbours fluctuate in a liquid, molecules diffuse in a liquid.

▶ Use a lattice model for the condensed phase.
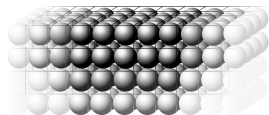
Lattice model of a condensed phase

- ▶ For the vapor, $G(T, p, N)$, whereas for the condensed phase we use $F(T, V, N)$. For the condensed phase, we can ignore the distinction to a good approximation. When the pressure is kept constant, the fluctuations in the volume are small, and *vice versa*.

- ▶ Only include short-range (nearest-neighbour) interactions. Two particles of type A have the bond energy, $w_{AA} < 0$, which is attractive.

- ▶ Regard the interaction energy as independent of the temperature. Very good approximation for covalent bonds, (c.f. we only regarded the ground state in the calculation of the electronic contribution to the partition function). Thus, good model for solids.

- ▶ The multiplicity, $W = 1$, since if a pair of particles swap position, we cannot distinguish the new arrangement from the old one (indistinguishable particles). Thus, $S = k_B \ln W = 0$.

- ▶ Contributions from vibrations (q_v) and rotations (q_r) in the liquid are ignored.

Lattice model of a condensed phase

Part 2

- ▶ Each particle on a lattice has z nearest neighbours, denoted the coordination number.
- ▶ Each bond has an energy of w_{AA}. Since a bond is shared between two particles, assign $\frac{w_{AA}}{2}$ to each particle.
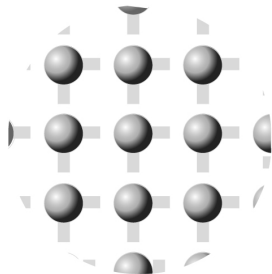
- ▶ The total internal energy, U, is thus

$$U = \frac{Nzw_{AA}}{2}$$

- ▶ The free energy (since $S = 0$),

$$F = U - TS = U = \frac{Nzw_{AA}}{2}$$

and the chemical potential, μ_c,

$$\mu_c = \left(\frac{\partial F}{\partial N}\right)_{T,V} = \frac{zw_{AA}}{2}$$

Vapor pressure

- At equilibrium, $\mu_c = \mu_v$,

$$k_B T \ln \frac{p}{p^o_{\text{int}}} = \frac{z w_{AA}}{2} \qquad \Rightarrow \qquad p = p^o_{\text{int}} e^{\frac{z w_{AA}}{2 k_B T}}$$
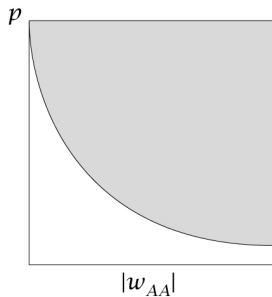
  where p is denoted the vapor pressure.

- Since (from the ideal gas law),

$$p = \left(\frac{N}{V} \right) k_B T$$

  the vapor pressure may be regarded as a measure of the density of the gas phase.

- If the bonds become stronger (note, $w_{AA} < 0$), the vapor pressure decreases (see figure).

- Also, if the temperature is increased, the vapor pressure increases.

Cavities in liquids and solids

▶ The energy to remove a particle (upper figure),
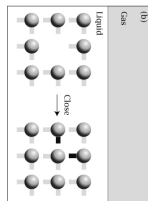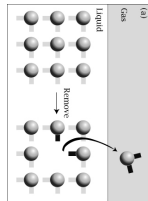
$$\Delta U_{\text{remove}} = -zw_{AA}$$

which is a positive energy.

▶ Note that half of ΔU_{remove} is assigned to to the particle leaving and half to the particles around the cavity.

▶ Another process of interest is the removal of a particle and the subsequent closure of the cavity (both figures),

$$\Delta U_{\text{remove+close}} = U(N-1) - U(N) = -\frac{zw_{AA}}{2}$$
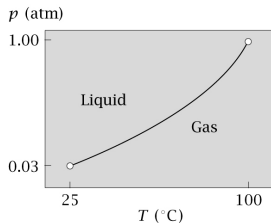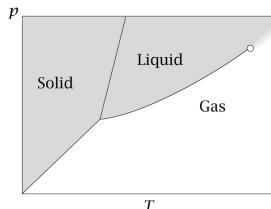
▶ This will be useful to model solvation (Ch. 16),

$$U_{\text{close}} = \frac{zw_{AA}}{2} \; ; \quad U_{\text{open}} = -\frac{zw_{AA}}{2}$$

$p(T)$ for phase equilibria

- ▶ Upper figure shows a phase diagram. Each line (phase boundary) shows a point (p, T) where two phases are equally stable (are in equilibrium).
- ▶ solid-gas (sublimation), solid-liquid (melting or freezing), liquid-gas (boiling or condensation)
- ▶ The lower figure shows the liquid-gas phase boundary for water.
- ▶ We will derive the slope of $p(T)$.

$p(T)$ for phase equlibria
Clapeyron equation

▶ Two points, (T_1, p_1) and (T_2, p_2), at equilibrium,

$$\mu_L(T_1, p_1) = \mu_G(T_1, p_1)$$
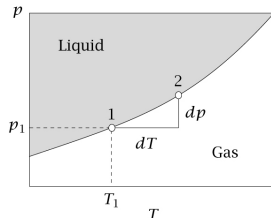
$$\mu_L(T_2, p_2) = \mu_G(T_2, p_2)$$

▶ Regard the chemical potential at point 2 as a perturbation of point 1,

$$\mu_L(T_2, p_2) = \mu_L(T_1, p_1) + d\mu_L(T, p)$$

$$\mu_G(T_2, p_2) = \mu_G(T_1, p_1) + d\mu_G(T, p)$$

▶ This leads to

$$d\mu_G(T, p) = d\mu_L(T, p)$$

$p(T)$ for phase equlibria

Clapeyron equation, part 2

▶ We regard μ as a function of (T, p),

$$d\mu(T, p) = \left(\frac{\partial \mu}{\partial T}\right)_{p,N} dT + \left(\frac{\partial \mu}{\partial p}\right)_{T,N} dp$$

▶ Use Maxwell relations (Table 9.1),

$$\left(\frac{\partial \mu}{\partial T}\right)_{p,N} = -\left(\frac{\partial S}{\partial N}\right)_{T,p} = -s \; ; \quad \left(\frac{\partial \mu}{\partial p}\right)_{T,N} = \left(\frac{\partial V}{\partial N}\right)_{T,p} = v$$

where s is the partial molar entropy and v is the partial molar volume.

▶ This leads to

$$d\mu_G = -s_G dT + v_G dp = d\mu_L = -s_L dT + v_L dp$$

$p(T)$ for phase equlibria

Clapeyron equation, part 3

▶ Rearrange as,

$$\frac{dp}{dT} = \frac{s_G - s_L}{v_G - v_L} = \frac{\Delta s}{\Delta v}$$

▶ At equilibrium: $\Delta \mu = \Delta h - T\Delta s = 0$,

$$\frac{dp}{dT} = \frac{\Delta h}{T\Delta v}$$

which is the Clapeyron equation.

$p(T)$ for phase equilibria

Clapeyron equation, part 4

▶ Since $v_G \gg v_L$,

$$\Delta v = v_G - v_L \approx v_G = \frac{RT}{p}$$
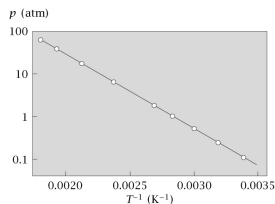
which leads to Clausius-Clapeyron equation,

$$\frac{d \ln p}{dT} = \frac{\Delta h}{RT^2}$$

▶ Alternative form by integration,

$$\int_{p_1}^{p_2} d \ln p = \int_{T_1}^{T_2} \frac{\Delta h}{RT^2} dT$$

$$\ln \frac{p_2}{p_1} = -\frac{\Delta h}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

▶ See figure for vapor pressure of benzene.

Refrigerators and heat pumps

- ▶ A refrigerator or a heat pump absorb energy from a cold place and releases it in a warmer place.
- ▶ Absorbs energy by boiling (breaking bonds) and releases energy by condensation.
- ▶ A fluid can be boiled a low temperature and recondensed at high temperature by controlling the pressure (compressing and expansion)
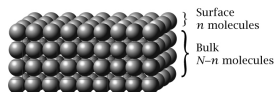- ▶ It is repeated as a thermodynamic cycle.
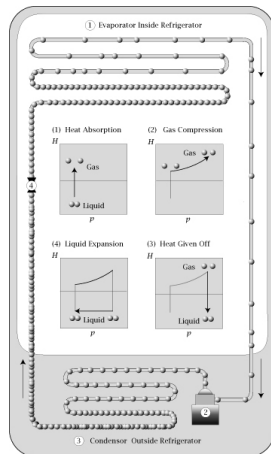
Equilibrium between molecules at the surface and in the bulk

Surface tension

- ▶ Surface - boundary between a condensed phase and a gas (or vapor)
- ▶ Interface - boundary between any two phases.
- ▶ Surface tension, γ,

$$dF = \cdots + \gamma dA$$

- ▶ Consider the lattice model in the figure: n molecules on the surface and $N - n$ molecules in the bulk.

} Surface n molecules

{ Bulk $N-n$ molecules

Equilibrium between molecules at the surface and in the bulk

Surface tension, part 2

► Surface atoms have $z - 1$ nearest neighbours,

$$U = \frac{z w_{AA}}{2} (N - n) + \frac{(z - 1) w_{AA}}{2} n = \frac{w_{AA}}{2} (Nz - n)$$

► The multiplicity, $W = 1$, thus the entropy $S = 0$ and $F = U$.

► The surface tension, γ,

$$\gamma = \left(\frac{\partial F}{\partial A} \right)_{T,V,N} = \left(\frac{\partial F}{\partial n} \right)_{T,V,N} \frac{dn}{dA} = \left(\frac{\partial U}{\partial n} \right)_{T,V,N} \frac{dn}{dA}$$

► The total area, $A = na$, where a is the area per particle,

$$\frac{dn}{dA} = \frac{1}{a} \; ; \quad \frac{\partial U}{\partial n} = \frac{-w_{AA}}{2}$$

Equilibrium between molecules at the surface and in the bulk

Surface tension, part 3

▶ The surface tension, γ, for this lattice model becomes,

$$\gamma = \frac{-w_{AA}}{2a}$$

▶ γ is a positive quantity ($w_{AA} < 0$).

▶ γ is the free energy required to move a particle from the bulk to the surface increasing the area with dA.

▶ Strong intermolecular forces gives high surface tensions, and the minimum possible surface (e.g. spherical drops).

Summary

- ▶ Lattice model for vaporization.
- ▶ For the question: why we have a vapour phase? (or why we have two coexisting phases?), we have to wait until chapter 25 on *Phase transitions*.
- ▶ Clausius-Clapeyron equation describes how phase equilibria depends on *p* and *T*.
- ▶ Refrigerator and heat pumps as examples.
- ▶ Lattice model for surface tension.

Exam Dec 2008 - Exercise 1 a-b

Vapour pressure

a) The vapour pressure for a pure solvent may be written as

$$p = p_{int}^o e^{\frac{\beta z w_{AA}}{2}}$$

Explain the various variables and constants in the equation. Which are the two fundamental approximations in this model for the vapour pressure, and what are the main limitations in each of the approximations?

b) What happens with the vapor pressure at high and low temperatures, and at strong and weak interactions between the liquid particles, respectively? Explain the results.